PB-217 486

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Federal Water Pollution Control Administration
Cincinnati, Ohio

January 1967

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Abstract

Pollution from acid mine drainage is a chronic problem. The current vigorous interest has led to a re-examination of the methods of measuring total acicidty, which are clearly based on the limited laboratory capabilities of prior years. Defined acid-metal mixtures containing iron(III), aluminum(III), iron(II), and hydrogen ion were reacted with sodium hydroxide under varying titration conditions. Results showed that at 25°C a reliable measure of the total acidity can be obtained by oxidizing iron(II) with hydrogen peroxide and stopping the titration at pH 7.3. Hydroloysis of Fe(III) and Al(III) was complete at pH 7.3 before formation of aluminate ion. Positive interference due to manganese and hardness can be held to a minimum by proper selection of sample volume. Acidity due to carbon dioxide is easily removed by aeration. The procedure was applied to the analysis of acid mine sample with added standards with recoveries of 98 to 103%; precision based on 5 or more determinations was of the order of 1%.

Key Words

Acid mine drainage Total acidity

Hydrolysis

Titration Iron(II) oxidation

DETERMINATION OF MINE-WASTE ACIDITY*

B. V. Salotto, E. F. Barth, M. B. Ettinger, and W. E. Tolliver**

Introduction

Acidity is variously defined as the capacity of a water to donate protons (1), as a property of a solution attributable to the presence of mineral acids (2), or the ability of a substance to accept and share an electron-pair with another substance, a base (3). The first definition is most useful in this discussion because protonic reactions occur in water systems, because the principle acidic components of acid mine wastes are protonic acids, and because a functional distinction can be made between these acids and other substances which also react with a strong base.

Total acidity as used in this paper means the amounts of base-consuming substances titrated under the stated conditions and is expressed as mg of sulfuric acid per liter. Conversion to the more common basis of calcium carbonate can be made by multiplying by 1.020.

Current methods depend on titration with strong base to an ill-defined end point under varying temperature conditions, either by use of indicators or electrometric instruments. With indicators, the chief interference is fading and impermanent end points. To improve end point detection, it has been recommended that samples be titrated at near

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*To be published in J. Environmental Science & Technology.

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boiling temperatures to hasten hydrolysis of metal salts (1), but, as will be shown, the determination of total acidity under hot titrating conditions presents more difficulties than it solves.

Experimental

Laboratory titrations were performed at about 25°C. Solutions were frequently checked, and either cooled or warmed to 25°C ± 2°. Determinations of total acidity were performed on an automatic titrator* which graphically recorded the titration curve of pH vs. volume of sodium hydroxide added. Results of total acidity determinations obtained by other methods were compared with auto-titrator results.

Ferric and ferrous iron, aluminum, and H^+ ion were investigated in this study because they are the predominant species present in acid mine drainage. Not considered were the several hydrolysis species of iron(III) and aluminum(III) which can exist in equilibrium with the parent species at low pH, or the bisulfate ion (HSO_4^-) in H_2SO_4 medium. The reactions with OH^- ion were assumed to proceed rapidly to the final hydrolysis products in the case of iron(III) and aluminum(III), and to the Na_2SO_4 product with H_2SO_4.

The following procedure was developed for determining mine waste acidity.

Apparatus

The titration assembly consisted of a properly calibrated pH meter**, 0.10 N NaOH titrant delivered from a 50-ml dog-leg burette, 150- and 250-ml beakers, and magnetic stirrer.

*Model D Auto-Titrator, E. H. Sargent & Co., Chicago, Ill.
**Beckman Zeromatic pH Meter, Fullerton, Calif.

Reagents and Chemicals

Carbon dioxide-free deionized water was used to prepare all solutions. Sodium hydroxide, 0.10 N, was standardized periodically with freshly prepared potassium hydrogen phthalate, and provision was made to protect the solution against atmospheric carbon dioxide. Iron(II) when present was oxidized by a 3 percent hydrogen peroxide solution. Potassium hydrogen phthalate and hydrated sodium borate chemicals were used to prepare the pH buffer solutions. A 1:5 hydrochloric acid solution was used to remove the coating of heavy metals from pH electrode surfaces.

Procedure

The pH meter was calibrated with pH 4 and pH 9 buffers at 25°C. Titrations were made on samples adjusted to 25°C ± 2°. Sample volumes were selected to provide a titration of 6 to 12 ml 0.10 N NaOH. Three ml of 3% H_2O_2 was added to the 100 ml sample in a 150-ml beaker and the sample was titrated rapidly to pH 7.3 end point with the aid of a magnetic stirrer.

In the absence of appreciable amounts of dissolved uncombined carbon dioxide, a slight fading will occur at pH 7.3 end point, which will be due to the slow absorption of CO_2 from the air and/or slow reaction of OH^- with $Al(OH)_3$. A rapid rise and fall of pH upon addition of NaOH titrant in titrating to pH 7.3 end point will indicate the presence of appreciable amounts of dissolved CO_2. If the sample contains appreciable amounts of dissolved CO_2, it should be removed by a 10- to 15-minute aeration before titration.

A standard acid-metals solution may be prepared to check the method. Any desired weight ratio of Fe(II), Fe(III), and Al(III), sulfate salts dissolved in standard H_2SO_4 solution may be used to provide a standard total acidity in the range encountered.

Results and Discussion

Comparison of Three Methods of Determining Total Acidity

Standard Methods (1) describes an acidity procedure for acid mine drainage samples using either an indicator or pH meter to denote the end point of the titration. The suggested end point is pH 8.3. To investigate the reactions involved in these procedures, six standard solutions of acid-metal mixtures, prepared from sulfate salts and sulfuric acid, were analyzed under cold (25°C) and hot (90°C) titrating conditions. The procedures employed were:

Auto-Titrator: Titration with 0.10 N NaOH to the last inflection point on the curve, under hot and cold conditions.

pH meter: Titration with 0.10 N NaOH to pH 8.3, under hot and cold conditions.

Phenolphthalein indicator: Titration with 0.10 N sodium hydroxide to indicator color change, under hot and cold conditions.

Total acidity of like samples was determined by each of the three above procedures. Results are shown in Table I. Each result represents the average of five analyses, performed by two analysts. The stoichiometric value for each standard solution is shown. Each standard solution determined by the auto-titrator procedure has two values reported. One value is calculated at the last inflection point of the curve, and the other computed at the arbitrary pH 8.3 end point.

The auto-titrator procedure, using the last inflection point of the curve as end point, gave values close to the stoichiometric value for each of the six hot or cold solutions.

The pH meter and phenolphthalein procedures yielded values different from the stoichiometric value, with the exception of ferric iron in the cold; and different values were obtained for hot and cold titrations of the same solution.

The auto-titrator data on Table I also show that the pH of the inflection point for the hot titrations are shifted 1 to 1.5 pH units lower than titration in the cold, as would be expected. Thus, selection of an 8.3 pH end point leads to an overestimation of the acidity due to ferric iron or aluminum; this positive error is further increased by a hot titration. Ferrous iron and manganese at pH 8.3 are not completely titrated and the total acidity will be underestimated at this arbitrary end point. However, for ferrous iron and manganese, under hot conditions, since the pH values at the inflection points are closer to the fixed pH 8.3, total acidity values approaching the stoichiometric are obtained.

For ferric iron the selection of end point pH or temperature of titration is not critical because the hydrolysis is rapid and the titration curve is very steep like that of a mineral acid. With aluminum the titration curve is not so steep and above pH 8 the formation of aluminate ion starts to consume base. Increased temperature shifts the inflection point lower and hastens the formation of aluminate ion. The pH meter and phenolphthalein indicator procedures show rapid fading of the end point in hot titrations of aluminum. The auto-titrator does not show this effect

because operator judgment is eliminated and the automatic titration is rapid.

The effect of temperature on the inflection point of the aluminum standard solution, and its relationship to the fixed pH value of 8.3 is illustrated in Figure 1. Aliquots containing equal milliequivalents of total acidity were titrated hot and cold so that the end point of each titration would be 8 ml 0.1 N NaOH. Figure 1 shows the pH value of the inflection point shifting from 7.4 at 25°C to 5.9 at 90°C.

Hydrogen Peroxide Oxidation of Ferrous Iron

Table I shows that, while the reaction of ferrous iron with strong base is complete in the cold, the last inflection point occurred at pH 9.7, well above the inflection points of ferric iron and aluminum. Under hot conditions the ferrous iron inflection point shifts to pH 8.8, which is close to the commonly used 8.3 end point, and good agreement is noted for ferrous iron between all three procedures under hot conditions.

The situation can be simplified by oxidizing ferrous iron to ferric with 3% hydrogen peroxide. Figure 2 shows the titration curves for ferrous iron, oxidized ferrous iron, and ferric iron with sodium hydroxide at 25°C. Each of the solutions contained equal milliequivalents of iron so that the total acidity at the inflection points would be the same. The completeness of the hydrogen peroxide oxidation can be seen from the fact that the oxidized ferrous curve is practically super-imposed on the ferric iron curve.

Ferrous iron was rapidly oxidized by excess H_2O_2 and possibly catalyzed by trace amounts of copper and manganese. Stumm[4] has shown

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that the rate of oxidation can be greatly influenced by the catalytic action of trace amounts of heavy metals such as copper and manganese.

The total acidity value of the ferrous iron solution was unaffected by H_2O_2 oxidation (see Figure 2). This is because an equal stoichiometric amount of base was required to neutralize both the oxidized iron solution and the unoxidized iron solution. The reaction:

$$Fe(II) + 2\ OH^- = Fe(OH)_2$$

requires two moles of base. The peroxide oxidation of ferrous iron and hydrolysis of ferric iron can be expressed by the following:

Oxidation:

$$2\ Fe(II) + H_2O_2 + 2\ H^+ = 2\ Fe(III) + 2\ H_2O, \text{ and}$$

Hydrolysis:

$$2\ Fe(III) + 6\ H_2O = 2\ Fe(OH)_3 + 6\ H^+,$$

The overall reaction being,

$$2\ Fe(II) + H_2O_2 + 4\ H_2O = 2\ Fe(OH)_3 + 4\ H^+$$

The oxidation of 1 mole of ferrous iron and subsequent hydrolysis of the 1 mole of ferric iron produced have a net requirement of 2 moles of base for the neutralization.

To determine the best end point pH which would represent the neutralization of Fe(II), Al(III), and H^+, standard acid-metal mixtures were titrated at 25°C ± 2°C on the auto-titrator with added H_2O_2. Aliquots from standards contained equal milliequivalents so that the end point of each titration would be 8.0 ml of 0.10 N NaOH. The same solutions were titrated without H_2O_2 addition so that the curves could be compared. The combined titration curves are shown in Figures 3a and 3b. As can be seen

in Figure 3b, which represents the titrations after peroxide oxidation, all the inflection points converge at about pH 7.3.

Titration of Standards to pH 7.3 With and Without Added H_2O_2

From the experiments shown in Table I and the hydrogen peroxide procedure shown on Figure 3b it appears that a fair assessment of the total acidity due to ferrous iron, aluminum, and hydrogen ion, can be obtained by oxidation of a sample with hydrogen peroxide to ensure all iron is in the ferric state and titrating to pH 7.3 with sodium hydroxide at 25°C. To confirm this, 7 standard acid-metal solutions were titrated with and without hydrogen peroxide oxidation using an end point of 7.3 on a pH meter. The results are shown in Table II. The data of Table II show that if a sample contains appreciable amounts of ferrous iron, low results will be obtained by this procedure in the absence of peroxide treatment. Oxidation with hydrogen peroxide and an end point of pH 7.3 at 25°C will give results agreeing closely with the stoichiometric values for all the solutions examined.

Two more standard acid-metal solutions of lower total acidity values than shown on Table I were prepared and titrated using the new procedure: Standard solution A contained 40 mg/l Fe(III), 50 mg/l Al(III), 200 mg/l Fe(II), dissolved in 0.010 N H_2SO_4. Standard solution B contained 80 mg/l Fe(III), 40 mg/l Al(III), 40 mg/l Fe(II) dissolved in 0.005 N H_2SO_4. The solutions were diluted and aliquots from these were titrated to establish the accuracy of the procedure at low total acidity range. Results are compared to duplicate analyses run concurrently on the auto-titrator and shown in Table III. No appreciable differences in results occurred using either the auto-titrator or pH meter in titrations

to pH 7.3 end point at 25°C with added H_2O_2. The results compare favorably with the stoichiometric total acidity values.

Interference of Mn, $Al(OH)_3$, Ca, and Mg

Auto-titration of several actual acid mine drainage samples produced titration curves showing a buffering effect due to the presence of manganese, $Al(OH)_3$, calcium, and magnesium. Laboratory mixtures of these metals produced curves similar to the acid mine samples. The four substances are all capable of reacting with base above pH 7.0, and the buffering effect which they produce is related to their concentrations in the sample. With added H_2O_2, the buffering effect is more pronounced, probably because of the non-stoichiometric reaction of divalent manganese with H_2O_2. In general, the buffering effect of these mixtures occurs well above the end point of pH 7.3, and no serious difficulty was experienced in differentiating this end point.

Standard solution A contained aluminum. Aliquots from this standard were mixed with aliquots taken from a manganese and a total hardness standard solution and titrated to the end point, pH 7.3, with added H_2O_2. The comparison between stoichiometric total acidity of the standard and the values found is shown in Table IV.

No serious error occurred in titrations of sample volumes containing approximately 1 mg Mn and/or 50 mg total hardness as $CaCO_3$ or less, at the aluminum level in the standard. Increased amounts of Mn, Ca, and Mg above these levels caused increasing positive errors. Not shown in the above table are titrations of sample volumes containing larger amounts of

aluminum but smaller amounts of Mn, Ca, and Mg which had no effect on the total acidity result.

Effect of Sample Size on Total Acidity Result

The total acidity result is dependent on the sample volume taken for analysis. The dependence is shown by the following test: Aliquots of 2.0 to 150 ml were taken from standard solution A and titrated to pH 7.3, and the total acidity found was plotted against total milliequivalents of acidity as H_2SO_4 present in the sample volume as shown in Figure 4. The dotted line in the figure represents the stoichiometric total acidity of the standard. The titration of sample volumes containing 0.60 to 1.25 milliequivalents produced results nearest the stoichiometric value. The largest negative deviation occurred in the titration of the largest sample size, approximately 3 percent from the ideal.

The slight negative interference resulting from the titration of a large sample size is believed due to the occlusion-effect of the mixed hydroxide floc which caused a portion of the iron to be unavailable for titration. The effect of occlusion is minimized when the milliequivalents of acidity lie in the range as shown in Figure 4.

The large, consistently positive error associated with a small sample volume is a result of large dilution factors; and the fact that in these dilute systems the pH change with increment of base added is rapid, and there is a bias to over titrate because of time lag in end point detection.

Negative interference is sometimes counterbalanced by the positive interference due to Mn, $Al(OH)_3$, Ca, and Mg. Figure 5 is similar to

Figure 4 except that aliquots were taken from an acid mine waste sample. The dotted line in the figure represents the total acidity value through the best milliequivalent range. The reversal of slope of the plot is due to the increasingly positive interference of larger and larger amounts of Mn, $Al(OH)_3$, Ca, and Mg in the portions titrated.

The selection of sample size to contain a favorable quantity of acidity provides the best means of overcoming objectionable levels of interferences.

Percent Recovery

Four acid mine samples collected from sampling locations in the Elkins, West Virginia acid mine drainage area were analyzed for acidity content by the new procedure. Manganese and total hardness were determined on two of the samples to ascertain the interference level. Five or more total acidity determinations were made on each sample to ensure reproducibility of results and to observe which sample volume contained the proper range of milliequivalents of acidity as well as minimum interferences. The field samples were diluted 10-fold and total acidities determined at low values. Total acidity values found on the basis of the above criteria and other pertinent data are shown in Table V.

To aliquots from two field samples, standard solutions, A and B, and 0.10 N H_2SO_4, were added, singly, and the mixtures were titrated to pH 7.3 with added H_2O_2 at 25°C ± 2°. Also, titrated were admixtures of diluted standards and diluted field samples. In each admixture, the total acidity found is compared to the expected value. The expected value was calculated on the basis of admixture of solutions of known

total acidity values, these being the stoichiometric value in the case of the standard, and the original analysis (Table V) in the case of the field sample. The comparison and percent recoveries of standards are shown in Table VI.

The data show that an accuracy of approximately 2% in the result can be achieved by titration to pH 7.3 in the high range, and 3% over the low range of total acidity, expressed as H_2SO_4. Precision is of the order of 1% based on 5 or more analyses of standards and field samples containing tolerable levels of interference and using suitable sample sizes.

Carbon Dioxide

Dissolved free carbon dioxide is titratable by strong base and will be included in the total acidity result if not removed by aeration before titration. In acid waters, CO_2 is dissolved and uncombined and will volatilize to an extent depending on the attainment of the atmospheric equilibrium. Samples containing appreciable amounts of dissolved CO_2 usually show rapid fading during the titration to pH 7.3.

It would be practical to consider CO_2 acidity as a volatile acidity easily removed by aeration in contrast to the non-volatile or permanent forms of acidity such as Fe(III), Al(III), and H^+.

Mention of products is for identification only and does not constitute endorsement by the Federal Water Pollution Control Administration or the U. S. Department of the Interior.

Acknowledgements

The authors wish to thank Lowell A. Van den Berg, Chief, Acid Mine Drainage Pollution Control Demonstration Program, for his cooperation in initiating this study, and Professor Werner Stumm, Harvard University, who gave them the benefit of his knowledge of iron chemistry in its relation to mine acidity.

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Table I

Determination of Total Acidity of Standard Acid-Metal Solutions by 3 Methods.
(Total Acidity Expressed as mg of H_2SO_4 per Liter)

Standard Acid-Metal Solution	Stoichiometric Total Acidity	Cold Titration (25°C)					Hot Titration (90°C)				
		pH at Inflection Point	Total Acidity Found	Percent Error	Total Acidity Calc. to pH 8.3	Percent Error	pH at Inflection Point	Total Acidity Found	Percent Error	Total Acidity Calc. to pH 8.3	Percent Error
AUTO-TITRATOR											
Fe(III) [a]	3615	7.2	3630	+0.4	3690	+2.1	6.4	3640	+0.7	3740	+3.5
Al(III) [a]	6434	7.4	6330	-1.6	6470	+0.6	5.9	6310	-1.9	7300	+13.5
Fe(II) [a]	2737	9.7	2630	-3.9	2460	-10.1	8.8	2680	-2.1	2650	-3.2
Mn(II) [b]	9808	10.3	9770	-0.4	7000	-29.6	9.6	9830	+0.2	8350	-14.9
Fe(III) + Al(III) [c]	5024	7.1	4970	-1.1	5110	+2.8	5.7	4940	-1.7	5490	+9.3
Fe(II) + Al(III) [c]	4585	8.3	4430	-3.4	4430	-3.4	7 2	4580	-0.1	4880	+8.6
pH METER TO pH 8.3											
Fe(III) [a]	3615	--	--	--	3720	+2.9	--	--	--	3870	+7.1
Al(III) [a]	6434	--	--	--	6730	+4.6	--	--	--	7740	+20.3
Fe(II) [a]	2737	--	--	--	2540	-7.2	--	--	--	2740	+0.1
Mn(II) [b]	9808	--	--	--	7100	-27.6	--	--	--	8390	-14.5
Fe(III) + Al(III) [c]	5024	--	--	--	5300	+5.5	--	--	--	5860	+16.6
Fe(II) + Al(III) [c]	4585	--	--	--	4710	+2.7	--	--	--	5360	+16.9
PHENOLPHTHALEIN INDICATOR											
Fe(III) [a]	3615	--	--	--	3750	+3.7	--	--	--	3850	+6.5
Al(III) [a]	6434	--	--	--	6790	+5.5	--	--	--	8050	+25.1
Fe(II) [a]	2737	--	--	--	2560	-6.5	--	--	--	2710	-0.9
Mn(II) [b]	9808	--	--	--	--[d]	--	--	--	--	--[d]	--
Fe(III) + Al(III) [c]	5024	--	--	--	5360	+6.7	--	--	--	6130	+22.0
Fe(II) + Al(III) [c]	4585	--	--	--	4990	+8.8	--	--	--	5220	+13.8

[a] 1000 mg/l in 0.02 N H_2SO_4

[b] 2747 mg/l in 0.10 N H_2SO_4

[c] 500 mg/l each in 0.02 N H_2SO_4

[d] Color change difficult to observe against brown precipitate background.

Table II

Effect of H_2O_2 Addition on Determination of Total Acidity by Titration to pH 7.3 End Point @ 25°C ± 2° on pH Meter. (Total Acidity Expressed as mg of H_2SO_4 per Liter)

Composition of Standard Acid-Metal Solutions.	Stoichiometric Total Acidity	Total Acidity Found	
		No H_2O_2	H_2O_2
Iron(III), 1000 mg/l, in 0.02 N H_2SO_4	3615	3630	3660
Al(III), 1000 mg/l, in 0.02 N H_2SO_4	6434	6260	6360
Iron(II), 1000 mg/l, in 0.02 N H_2SO_4	2737	2330	2610
Iron(III) + Al(II) + Iron(II) 600 mg/l 300 mg/l 100 mg/l in 0.02 N H_2SO_4	4374	4390	4400
Iron(III) + Al(III) + Iron(II) 200 mg/l 400 mg/l 400 mg/l in 0.02 N H_2SO_4	4391	4280	4340
Iron(III) + Al(III) 500 mg/l 500 mg/l in 0.02 N H_2SO_4	5024	4970	4970
Iron(II) + Al(III) 500 mg/l 500 mg/l in 0.02 N H_2SO_4	4585	4250	4470

Table III

Comparison of Total Acidity Results Obtained by Auto-Titrator and by pH meter Instruments, by Titration to pH 7.3 End Point with Added H_2O_2 @ 25°C ± 2°.

(Total Acidity Expressed as mg of H_2SO_4 per Liter)

Standard	Stoichiometric Total Acidity	Total Acidity Found	
		Auto-Titrator	pH Meter
Solution A	1210	1200	1200
Solution B	740	745	735
Diluted Solution:			
1/10 Dilution Solution A	121	124	124
1/4 Dilution Solution B	185	184	186

Table IV

Interference of Manganese and Total Hardness on Total Acidity Result of Standard Acid-Metal Solution A.

(Total Acidity Expressed as mg per Liter of H_2SO_4)

I. Manganese

Mn*	Stoichiometric Total Acidity Solution A	Total Acidity Found	Percent Error
0.00	1210	1200	-0.8
0.25	1210	1200	-0.8
0.85	1210	1200	-0.8
1.00	1210	1210	0.0
1.40	1210	1220	+0.8
5.60	1210	1250	+3.3
7.00	1210	1300	+8.3

II. Total Hardness (Solution composed of equal weight mixtures of Ca & Mg)

As $CaCO_3$*	Stoichiometric Total Acidity Solution 4	Total Acidity Found	Percent Error
30	1210	1200	-0.8
60	1210	1210	0.0
75	1210	1260	+4.1
90	1210	1320	+9.1
180	1210	1440	+11.9

III. Manganese plus Total Hardr ss

Mn*	$CaCO_3$*	Stoichiometric Total Acidity Solution A	Total Acidity Found	Percent Error
0.60	8.0	1210	1200	-0.8
5.00	72	1210	1290	+6.6

*mg added to aliquot

Table V

Analysis of Acid Mine Waste Field Samples*

(Total Acidity Values Obtained by Titration to pH 7.3 End Point with Added H_2O_2 @ 25°C ± 2° on pH Meter and are Expressed as mg of H_2SO_4 per Liter)

Field Sample	Average Total Acidity Found	Manganese Found Mn, mg/l	Total Hardness Found $CaCO_3$, mg/l
1	1410	10	730
1/10 Dilution 1	150		
2	690	5	500
1/10 Dilution 2	74		
3	1460	--	--
1/10 Dilution 3	150		
4	620	--	--
1/10 Dilution 4	68		

*Collected at various locations in the Elkins, West Virginia acid mine drainage area.

Table VI

Percent Recovery of Standards

(Total Acidity Values Obtained by Titration to pH 7.3 End Point with Added H_2O_2 @ 25°C ± 2° on pH Meter and are Expressed as mg of H_2SO_4 per Liter)

Admixture		Total Acidity		Percent Recovery	Percent Error
Acid-Mine-Waste Field Sample	Standard Added	Found	Calculated		
1	Soln. A	1300	1300	100.0	0.0
1	Soln. B	930	930	100.0	0.0
1	0.1 N H_2SO_4	2630	2640	99.6	-0.4
1/10 Dilution 1	1/4 Dil. Soln. B	167	168	99.4	-0.6
2	Soln. A.	1070	1060	100.9	+0.9
2	Soln. B	732	715	102.4	+2.4
2	0.1 N H_2SO_4	2170	2160	100.5	+0.5
1/10 Dilution 2	1/4 Dil. Soln. B	134	130	103.1	+3.1

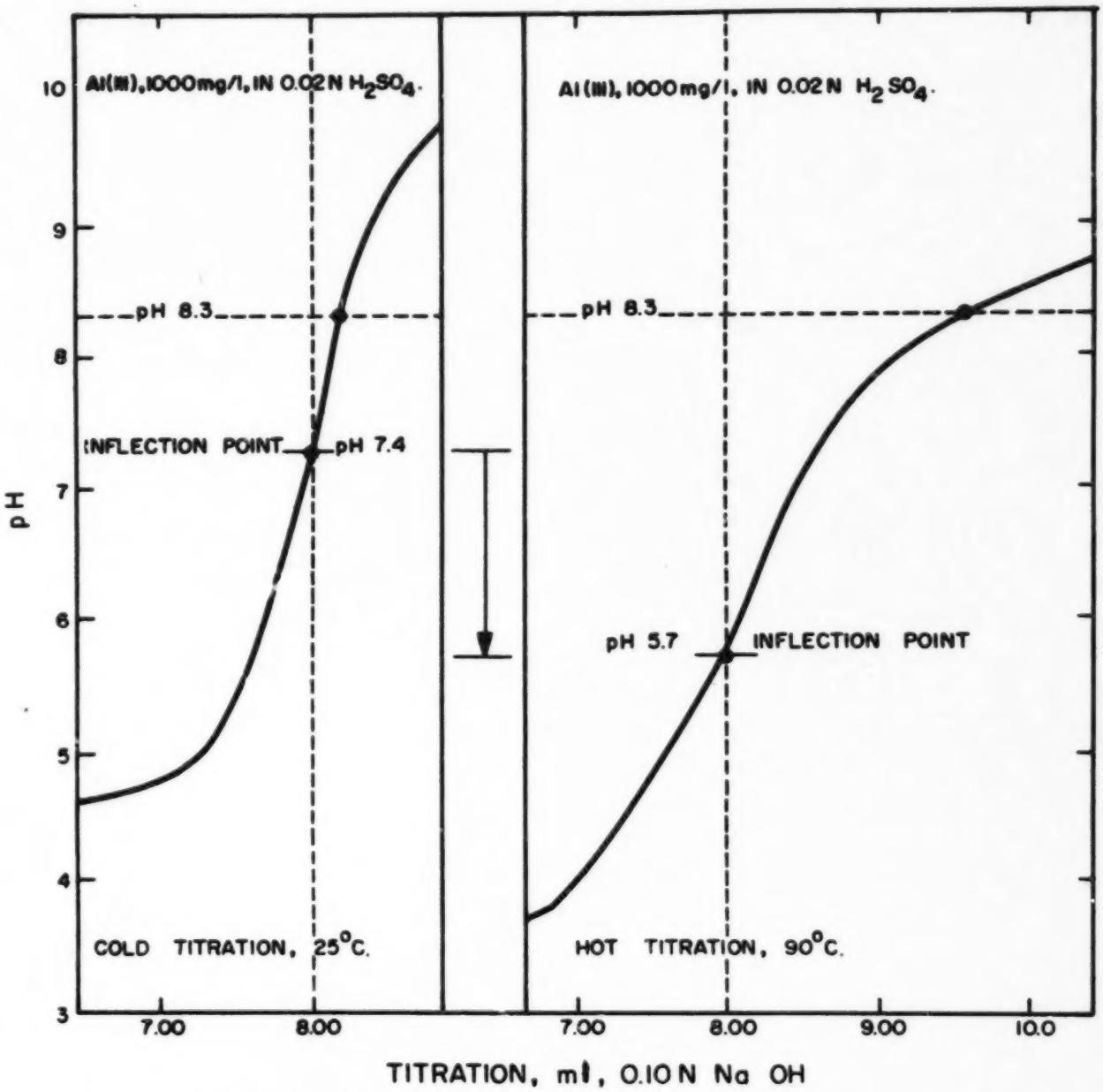

Figure 1. Shift of inflection point as a result of titrating at a higher temperature. Equal milliequivalents titrated. (H_2SO_4 inflection points not shown.)

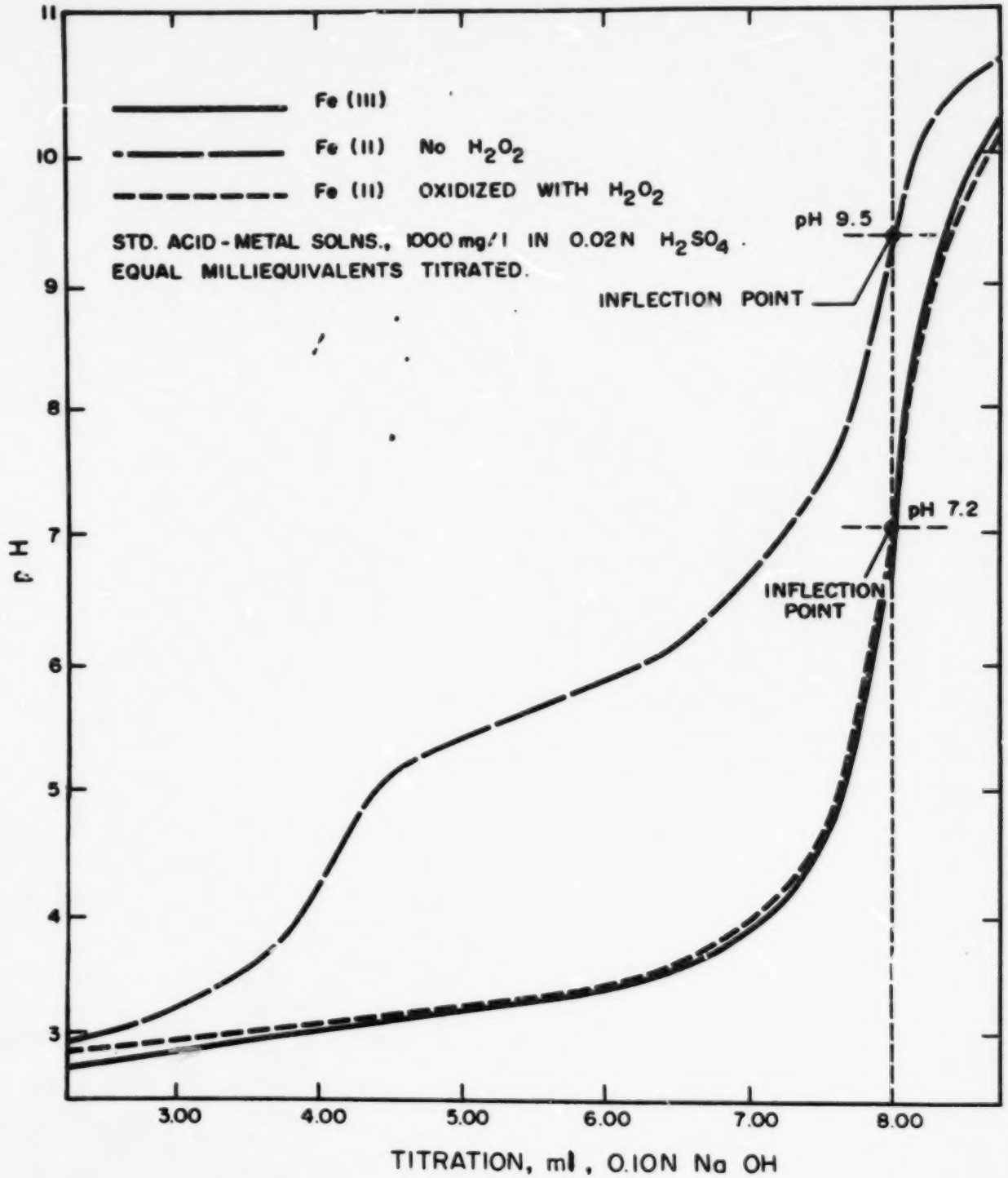

Figure 2. Titration curves of iron (II) and iron (III) solutions. effect of H_2O_2 addition.

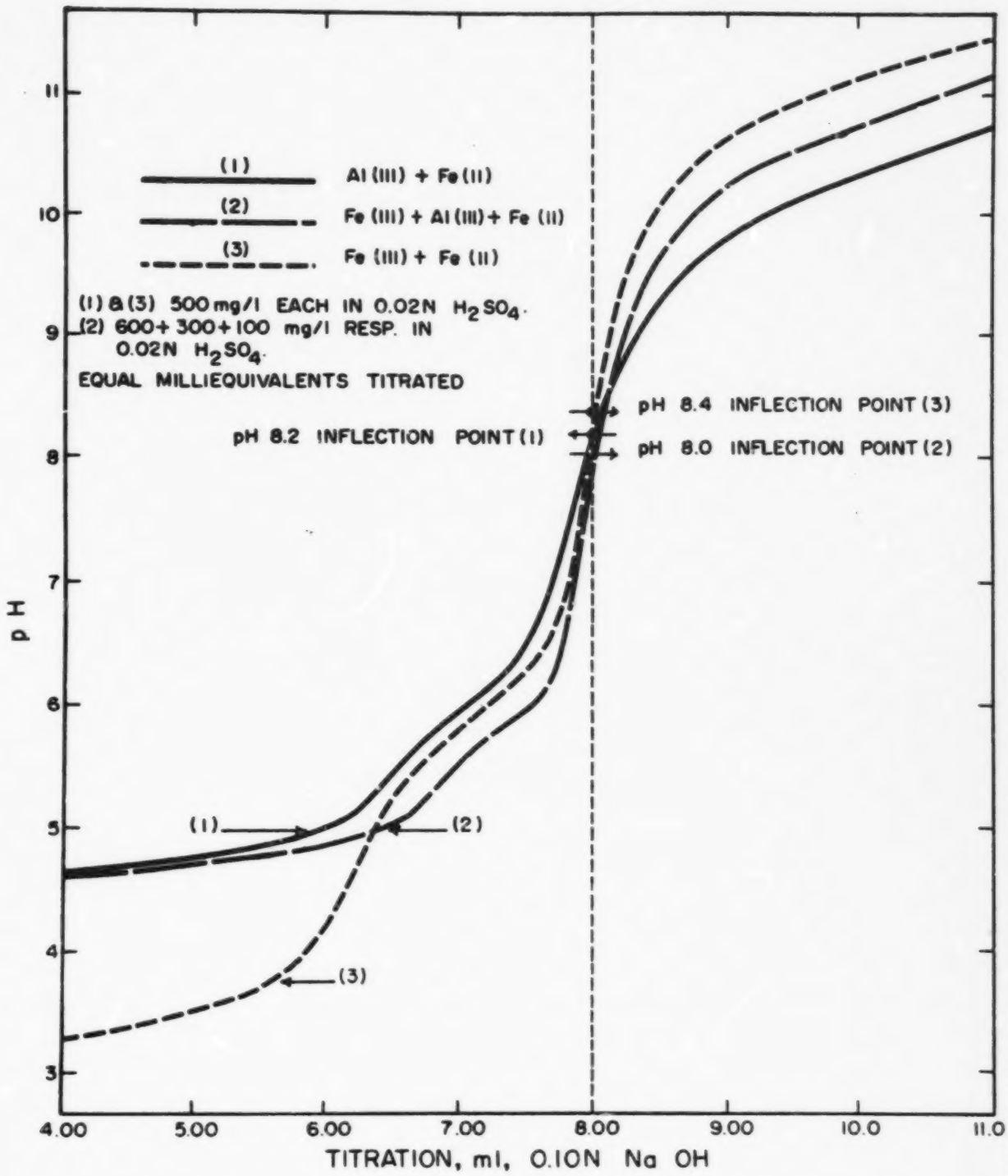

Figure 3a. Titration curves of acid-metal mixtures, not treated with H_2O_2.

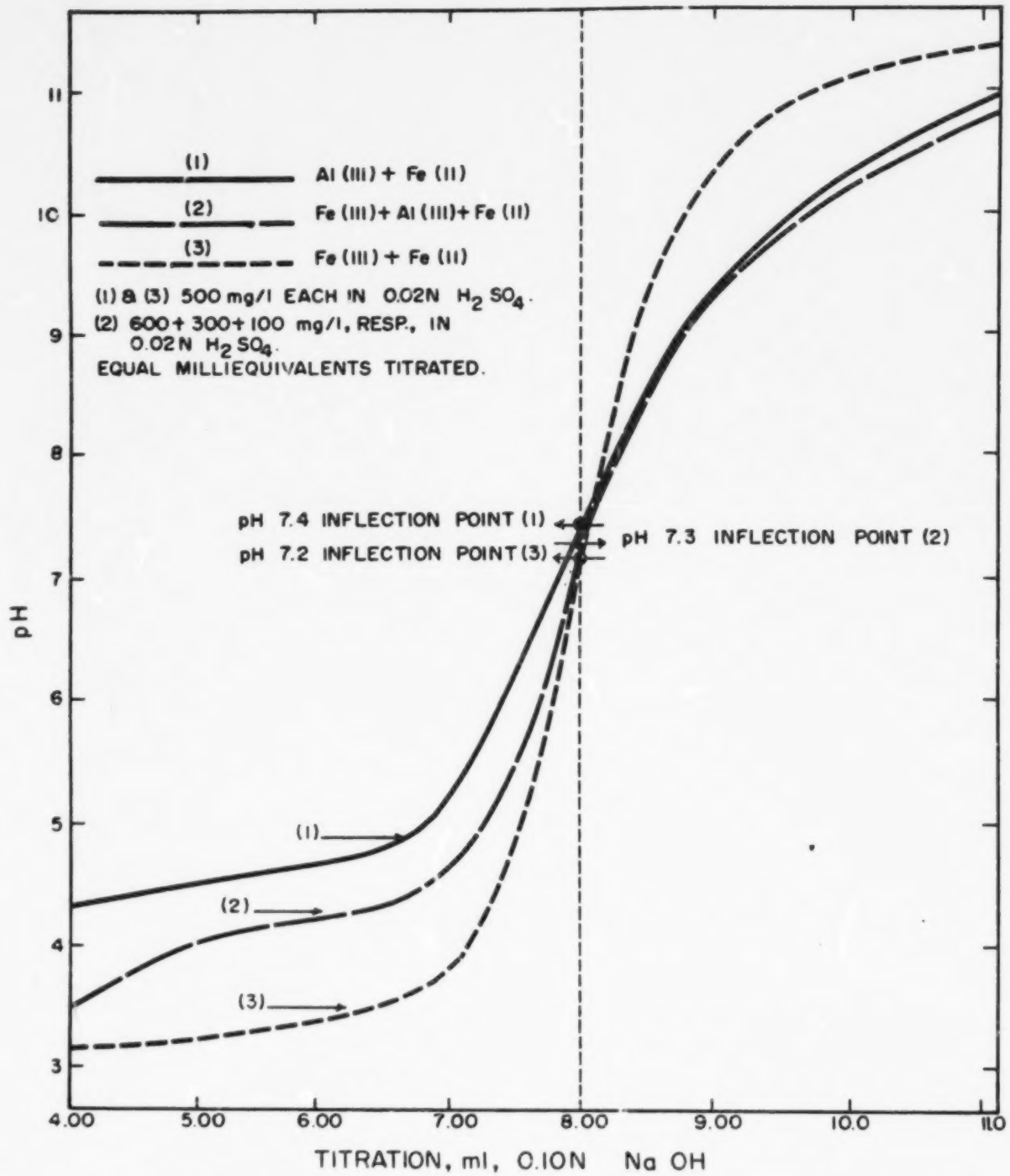

Figure 3b Titration curves of acid-metal mixtures, treated with H_2O_2.

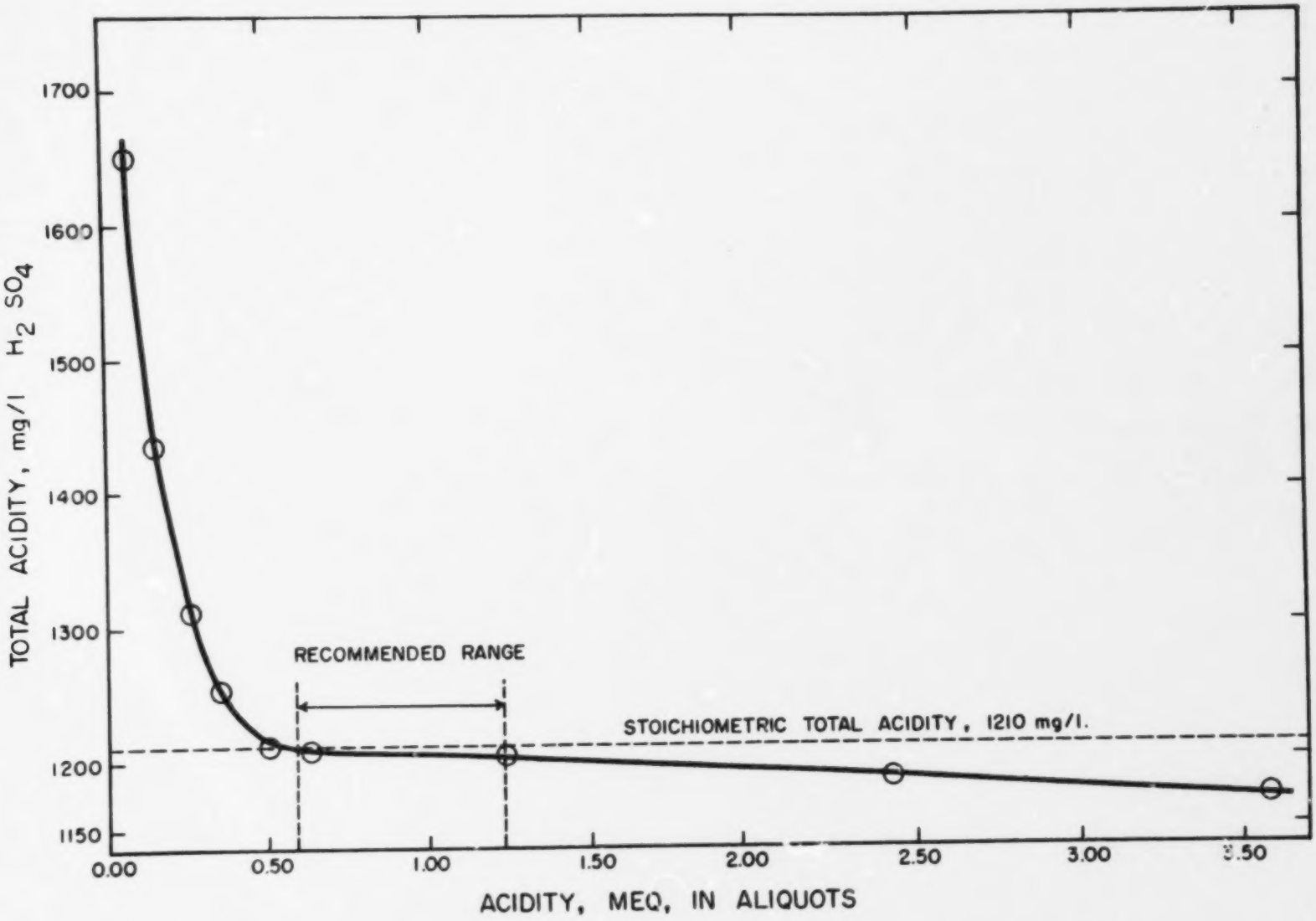

Figure 4. Total acidity found versus milliequivalents titrated, standard solution, A.

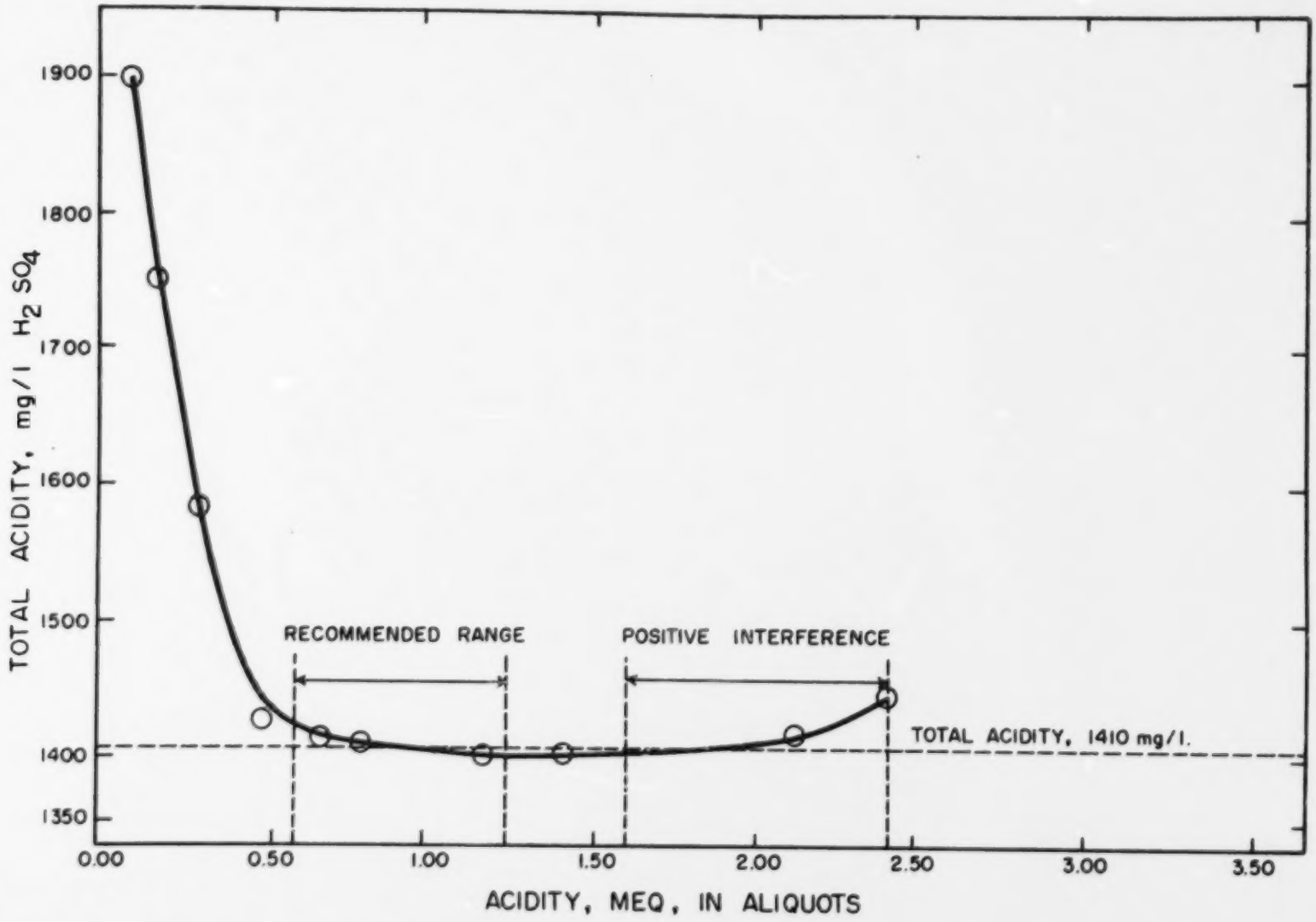

Figure 5. Total acidity found versus milliequivalents titrated, field sample 1.